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INSECTICIDE RESIDUES ON FORAGE CROPS

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The use of insecticides for the control of insects on forage and other crops where a portion of the vine or top may be fed is a well-established practice. The level of insecticide residues remaining in the crops is of importance because of the possible deposition of the insecticide in the fat or secretion in the milk of animals.

Dobson, Thornberry and Belling (4)^{1/} reported the rapid rate of loss of phorate residues on alfalfa. When analyzed by the cholinesterase inhibition method, residues of approximately 400 parts per million declined in 14 days to nonmeasurable levels. No adverse effects were observed in cattle that were fed the treated hay. Huddleston and Gyrisco (15) found, when carbaryl in oil was applied at 1 lb. per acre, there was a rapid loss of residue from alfalfa and red clover. The original deposit of carbaryl on both crops was not as high as was DDT applied at the same rate. Reynolds and coworkers (24) in their work with trichlorfon on alfalfa found, when 1 lb. per acre was applied, that the residue after 4 days was less than 1 p.p.m. and was not measurable at 10 days after application.

A comprehensive survey of four chlorinated insecticides was done by members of ENT-ARS-USDA (5) in 1956, 1957, and 1958 to determine the residue in fat of cattle grazing on insecticide-treated range land (following standard cattle management practices). The residues on forage samples collected 1 day after treatment were below 4 p.p.m.; in some of them, 0.4 p.p.m. remained after 34 days.

According to Dickason and Terriere (3), early season application of granular aldrin and heptachlor at 1 lb. per acre to red clover did not result in measurable residues at harvesttime when analyzed by a total chloride method. When Gyrisco and Huddleston (13) applied aldrin, dieldrin and endrin to alfalfa and measured the residues on fresh and cured hay, they found that dieldrin was more persistent than endrin and endrin more persistent than aldrin.

In a study of dieldrin applied at dosages up to 1 lb. per acre in irrigated pastures Smith and others (27), employing a colorimetric procedure, found the initial deposit from granular applications of dieldrin did not

^{1/} Underscored numbers in parentheses after the authors' names refer to Literature Cited at end of this report.

exceed 1.2 p.p.m. and that the residues persisted for 12 weeks. Where dieldrin emulsions were applied, rate of loss curves were obtained with a rapid loss in the first 2 weeks, with residues remaining up to 16 weeks. Fishgang and Shaw (6) applied 1 and 1-1/2 lb. of granular diazinon per acre to alfalfa, birdsfoot trefoil, and ladino clover and reported that residues of less than 0.01 p.p.m. were found 2 months later. In comparing the rate of loss of azinphosmethyl from red and ladino clover, Shaw, Smith, and Fishgang (26) reported the initial deposits were similar, but the rate of disappearance from ladino clover was faster than from red clover. Hardee and others (14) found the initial deposit of methyl parathion, methoxychlor, heptachlor, and lindane was higher and the rate of loss was slower on timothy and alfalfa than on birdsfoot trefoil and red clover.

Due to the variability in analytical methods, the lower limit of sensitivity as reported by the various authors differs considerably, particularly in the case of the chlorinated hydrocarbon insecticides. The analytical methods now available increase sensitivity approximately 100-fold over methods previously available.

This report presents the results of analyses made of red clover, lima bean straw, and range grass from 1957 through 1964 for residues of one carbamate, five chlorinated hydrocarbons, and eight organic phosphate materials. Not all of these insecticides were applied to each crop during the 8-year study.^{2/} The data reported include the insecticides applied, rate per acre, method of application, the analytical methods, and residues found at different time intervals after application.

FIELD PROCEDURES

Red Clover

The plots were generally 50 by 50 ft. in size. Residue samples of fresh green clover varying from 2 to 9 lb. were taken by random sampling of 6 to 8 locations per plot. Approximately 4 sq. ft. per location were sampled. The clover was stored in a refrigerator for a short time and then shipped with dry ice by air express to the laboratory and kept frozen until analyzed.

Lima Bean Straw

Field plots ranged from 10 by 158 ft. to 20 by 100 ft. in size. One to two pounds of dry straw was obtained from each plot at the time of threshing the dry lima beans. The central 1/100 of an acre was threshed from each plot and there were six replicates of each treatment. The dry straw was shipped by air express and at the laboratory the samples were frozen until analyzed. Granular insecticides were applied in the soil with and behind the seed at planting. Twenty gallons of foliage spray per acre was applied with a power sprayer using two nozzles per row at 125 pounds pressure.

^{2/} Cooperating entomologists, Joseph Wilcox in California, Frank Cowan and Fred Skoog in Montana, and H. W. Prescott in Oregon applied the insecticides and did the field sampling.

Range Grass

The range grass plots varied from 5 to 320 acres in size. A Lawn-O-King[®] 3/4 reel-type power mower, with a front-mounted catcher was used for cutting samples from all plots. For aerial applications the transects (samples) were cut at right angles to the line of flight. Two or more transects, depending on the size of the plots and the number of samples needed, were cut, mixed together and held at 0°F. All samples were packed with dry ice and shipped via air express and held in frozen condition until analyzed.

INSECTICIDES ANALYZED

The following insecticides were determined: aldrin; azinphosmethyl (Guthion[®]); Bomyl[®] (dimethyl 3-hydroxyglutaconate dimethyl phosphate); carbaryl (Sevin[®]); diazinon; dieldrin; dimethoate; disulfoton; heptachlor; heptachlor epoxide (1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methano=indan); naled (Dibrom[®]); phorate; toxaphene; and trichlorfon (Dylox[®]). Dieldrin and heptachlor epoxide were not applied as such, but resulted from the degradation of aldrin and heptachlor, respectively.

LABORATORY PROCEDURES

Prior to analysis the forage samples were cut into approximately 1-inch lengths by passing them through a lawn mower-type cutter. After cutting, the samples were well mixed and suitable portions weighed out for analysis.

Solvents were distilled in an all-glass apparatus before use, except the reagent grade isopropyl alcohol which was used as received.

Red Clover

Aldrin and Dieldrin

Three-hundred grams of red clover were tumbled with a 2-to-1 mixture of hexane and isopropyl alcohol and filtered, and the isopropyl alcohol was removed by repeated washing with distilled water. The washed extract was dried by filtration through anhydrous sodium sulfate. A portion of the extract was concentrated to 35 ml. and chromatographed through a hexane pre-washed Attasol[®]-Hyflo Super Cel[®] (2:1) column. The aldrin was eluted from the column with hexane and determined by the method of O'Donnell and others (19).

An additional portion of the extract was concentrated and chromatographed through a hexane pre-washed column of a homogeneous mixture of equal amounts of 60-mesh Florisil[®]: magnesium oxide: Hyflo Super Cel: Columbia[®] activated carbon. The column was eluted with 95:5 hexane:ethyl ether. The dieldrin content was measured by the method of either O'Donnell, Johnson and Weiss (20) or Cueto (2). In the samples analyzed by the method of Cueto, the eluate from

3/ Mention of a proprietary product in this publication does not constitute a guarantee or warranty of the product by the U. S. Department of Agriculture and does not imply its approval by the Department to the exclusion of other products that may also be suitable.

the column was treated by shaking with a small amount of Nuchar C-190-N[®], followed by filtration and the washing of the filter with hexane. The method of Cueto was modified by using zinc chloride in acetone and dissolving the colored complex in glacial acetic acid, instead of a mixture of glacial acetic acid and acetic anhydride.

Carbaryl

For the analysis of carbaryl, portions of the chopped sample were tumbled with chloroform and the extracts were filtered through anhydrous sodium sulfate. Where the samples were analyzed by the method of Miskus, Gordon and George (18), a portion of the extract was concentrated to 25 ml. and chromatographed through a dry 60-mesh Florisil column. The column was eluted with chloroform. In those samples analyzed by the method of the Union Carbide and Chemical Corp. (28), the suggested cleanup column was modified by the addition of layers of Attaclay[®] and aluminum oxide.

Heptachlor and Heptachlor Epoxide

These residues were determined on the same portion of the plant extract. Three methods of extraction and analysis were used. In one method, the samples were extracted by tumbling with hexane, filtered through sodium sulfate, and chromatographed through a 60-mesh Florisil column. The heptachlor was eluted from the column with petroleum ether followed by removal of the epoxide with a 3:1 mixture of benzene:petroleum ether. The heptachlor content was determined by the method of Ordas, Smith and Meyer (21) and the epoxide by the method of Gannon and Decker (7).

In the second method of analysis, the samples were extracted by tumbling with a 2:1 mixture of hexane:isopropyl alcohol. The extracts were filtered and washed free of isopropyl alcohol and subjected to the same cleanup procedures as above. In the method of Gannon and Decker (7), the Davidow reagent was used instead of the specified Polen-Silverman reagent.

In the third method of analysis, the samples were blended with a 2:1 mixture of hexane:isopropyl alcohol and filtered, the isopropyl alcohol was removed by washing, and the extracts were dried with sodium sulfate. The dried extract was chromatographed through a 60-mesh Florisil column overlaid with Norit A[®] and the combined heptachlor and epoxide were eluted with 94:6 hexane:ethyl ether. The residue content was determined by the more sensitive means of gas chromatography utilizing electron capture detection by the method of Lovelock and Lipsky (16).

Toxaphene

For the analysis of the toxaphene residues, the samples were extracted by tumbling with hexane and the extract was filtered through anhydrous sodium sulfate. The extract was shaken with 2 g. of Florex[®], filtered, washed with hexane, and concentrated, and the toxaphene residue was calculated from total chlorine analysis determined by the method of Phillips and DeBenedictis (23).

Azinphosmethyl

Azinphosmethyl samples were tumbled with hexane:isopropyl alcohol (2:1), and the isopropyl alcohol was removed by washing with distilled water. A portion of the extract was chromatographed through a dry column of aluminum oxide and the column eluted with benzene. The azinphosmethyl content of the samples was determined by the method of Mengher and coworkers (17).

Dimethoate

The samples were extracted by blending with methylene chloride, adding Celite® and anhydrous sodium sulfate after blending, and then centrifuging. The centrifuged extract was filtered, concentrated to approximately 10 ml. and chromatographed through a methylene chloride pre-washed Florisil column overlaid with Nuchar-C-190-N. The column was eluted with methylene chloride. The dimethoate residues were determined by the colorimetric method of George and coworkers (9).

Other lima bean straw samples were blended with chloroform and filtered, and the extract shaken with a mixture of Columbia activated carbon and 200-mesh Florisil, filtered, and concentrated to approximately 50 ml. The extract was shaken with 2 g. of Nuchar-C-190-N:Attaclay (2:1), filtered, and carefully evaporated to dryness. The dimethoate content was determined by the total phosphorus method of Gigger (11) as modified by George (8).

Disulfoton

For the determination of the disulfoton content of lima bean straw, the samples were blended with chloroform, anhydrous sodium sulfate was stirred into the blended sample, and the chloroform layer was allowed to separate and was decanted through a filter. Two cleanup and oxidation methods were used.

A portion of the extract was gravity filtered through a sintered glass funnel containing sodium sulfate and a chloroform-washed and air-dried mixture of aluminum oxide:Nuchar-C-190-N:200-mesh Florisil (1:1:2). The cleaned-up extract was concentrated and oxidized according to the procedure of Patchett and Batchelder (22). The disulfoton residue content was determined by the cholinesterase inhibition procedure of Hensel and associates^{4/} modified to include a 1-hour incubation time instead of the suggested 2 hours.

The other procedure used a portion of the extract shaken with 6 g. of a mixture of equal amounts of Nuchar-C-190-N and magnesium oxide, filtered, concentrated to about 5 ml., and oxidized with perbenzoic acid according to the method of Giang and Schechter (10). The disulfoton residue content was determined as in the first procedure.

^{4/} Hensel, J., Hewitt, H. E., Sheets, U. M., and Scott, R. C. 1954. Microestimation of demeton residues. Presented before the Div. of Agr. and Food Chem., Amer. Chem. Soc. March 1954.

Phorate

The lima bean straw was blended with chloroform, filtered, and the filtrate dried with sodium sulfate. A portion of the extract was diluted to 100 ml. with chloroform and washed twice with 10 ml. of 75 percent sulfuric acid followed by 3 water washes and a saturated sodium chloride wash. The extract was cleaned up by chromatographing through a dry column of 3:1 acid-washed Nuchar-C-190-N:Hyflo Super Cel. The phorate content was determined by the method of Giang and Schechter (10).

Trichlorfon

In the analysis of trichlorfon residues the straw samples were blended with chloroform and filtered through anhydrous sodium sulfate. A portion of the extract was evaporated to a small volume and transferred to a test tube containing 1/2 ml. of water. The chloroform phase was evaporated and the trichlorfon residues determined by the inhibition procedure of Hensel and associates.^{5/}

Range Grass

Bomyl

The sample of range grass was ground dry in a blender, transferred with chloroform to a tumbling jar, allowed to steep for 24 hours, tumbled, and the extract removed by filtration. A portion of the extract was concentrated to 30 ml. and chromatographed through a dry column of a mixture of equal parts Nuchar-C-190-N, aluminum oxide, magnesium oxide-Hyflo Super Cel (1:1) and 60-mesh Florisil. The column was eluted with chloroform and the sample evaporated to dryness. For original portions of 20 ml. or less, the samples were shaken with 2 g. of the above mixture rather than chromatographed through the column. The Bomyl residue was determined by the total phosphorus method of Saliman (25).

Carbaryl

The range grass samples were extracted in the same manner as the red clover samples. A portion of the extract was treated with the coagulating mixture of Miskus, Gordon, and George (18), evaporated to about 15 ml., and shaken with an Attaclay-aluminum oxide mixture (1:1), filtered, and the carbaryl residues were determined by the method of the Union Carbide and Chemical Corp. (28).

Diazinon

The samples were tumbled with petroleum ether and the extract was filtered through sodium sulfate. No cleanup procedure was required. The method for the determination of sulfur as published by Gigger (12) was used in the final analysis.

^{5/} See footnote No. 4.

Dimethoate

The dimethoate residue was determined by the same procedures as previously described for the analysis of Bomyl.

Naled

Samples were blended with water and transferred with petroleum ether to a tumbling jar. Following the addition of concentrated hydrochloric acid to the jar in the ratio of 4 ml. of acid per 100 g. of sample and enough petroleum ether to make a final ratio of 4 ml. per g. of sample, the samples were tumbled, anhydrous sodium sulfate was added, and the petroleum ether phase was allowed to separate and was decanted through a filter. A portion of the petroleum ether extract was added to a test tube containing 1/2 ml. of water, and the solvent phase was removed by evaporation. The naled content was determined by a cholinesterase-inhibition method described by the California Spray-Chemical Corp. (1) as modified by the procedure used in the disulfoton method.

PERCENTAGE RECOVERY

To determine the recovery of the various insecticides, known amounts of each insecticide were added to untreated or check samples before extraction. In addition, known amounts of the metabolites dieldrin and heptachlor epoxide were added to certain samples. The average percentage recovery of insecticides added to nontreated check samples of the three forage crops is presented in table 1.

Table 1.-Recovery of known amounts of insecticide added to non-treated check samples

Insecticide added	Average recovery		
	Red clover	Lima bean straw	Range grass
	Percent	Percent	Percent
Aldrin - - - - -	89.3	--	--
Azinphosmethyl - - - - -	--	80.0	--
Bomyl - - - - -	--	--	81.4
Carbaryl - - - - -	90.7	--	81.7
Diazinon - - - - -	--	--	84.5
Dieldrin - - - - -	--	95.3	--
Dimethoate - - - - -	--	88.6	81.1
Disulfoton - - - - -	--	85.0	--
Heptachlor - - - - -	80.0	--	--
Heptachlor epoxide - - - - -	88.3	--	--
Naled - - - - -	--	--	100.8
Phorate - - - - -	--	95.1	--
Toxaphene - - - - -	109.2	--	--
Trichlorfon - - - - -	--	116.1	--

DISCUSSION

During the period from 1957 through 1964, approximately 500 samples of forage crops were analyzed for insecticide residues. The major portion of these samples consisted of range grass experimentally treated for grasshopper control. Samples of red clover treated for root borer control and of lima bean straw treated for control of certain foliage-feeding insects were also analyzed. The presence of certain insecticide residues on the above-mentioned forage could result in the deposition of these materials in the fat of the animals and the possible secretion of the pesticides, or their metabolites, in the milk. In results of analyses employing older procedures (prior to gas chromatography and more sensitive colorimetric methods), the lower level of accuracy of the analytical method is presented where the residue levels found were equal to or less than the lower limit.

Red Clover

Table 2 presents the residue levels found when red clover was treated with one carbamate and three chlorinated hydrocarbon insecticides. Where 0.8 to 2.7 lb. of aldrin were applied, either as a granular material or as a dust 66 to 83 days before harvest, no measurable residues of aldrin or its metabolite dieldrin were found on the red clover when the samples were analyzed by colorimetric methods. When carbaryl was applied as a dust at 1.5 lb. per acre 49 days before harvest, the residue ranged from 0.20 to 0.47 p.p.m. Residues on the same plots were less than 0.10 p.p.m. 65 days after application.

The application of heptachlor either as the granular material or as a dust resulted in measurable deposits of heptachlor and its metabolite, heptachlor epoxide, when determined by gas chromatography. No deposits in excess of the lower limit of accuracy of the analytical methods were found by colorimetric analysis. Red clover samples taken 51 days after treatment with either 0.25 or 1.00 lb. of heptachlor per acre, as granules, did not contain measurable deposits when analyzed by colorimetric methods. When 0.75 lb. of granular heptachlor was applied, residues of 0.14 and 0.01 p.p.m. of heptachlor and heptachlor epoxide were found 201 days after application, because of the increased sensitivity of the newer gas chromatographic methods of analysis.

The aerial application of heptachlor granules at 1.3 lb. per acre resulted in residues of 0.016 p.p.m. heptachlor and 0.004 p.p.m. heptachlor epoxide 236 days after application, when analyzed by gas chromatographic techniques. When 1.5 lb. of heptachlor, as granules, were applied by aircraft and samples taken 77 days after application, no measurable residues were found by colorimetric techniques. When the same amount was applied by aircraft as a dust and sampled at 77 days after application, residues of 0.18 p.p.m. of heptachlor were found by colorimetric methods. No measurable epoxide was found. The increase in heptachlor residue is possibly explained by the nature of the formulation applied. The granular material tends to scatter through the foliage while the dust formulation adheres to the foliage. The presence of residues of heptachlor or heptachlor epoxide at harvesttime prohibits application of the rates and formulations tested where the forage may be consumed by lactating animals or animals being finished for slaughter. The significance of the lower level deposits, such as 0.004 p.p.m., has not been evaluated.

Table 2.-Insecticide residues on red clover

Formulation and method of application	Pounds per acre (actual)	Days since last application	Residues in parts per million ^{1/}		Analysis
			Insecticide	Metabolite ^{2/}	
Aldrin:					
Granules-power pack - - - - -	0.8	83	3/ 0.15	<0.15	Color.
Do. - - - - -	1.3	83	--	< .15	Do.
Do. - - - - -	1.5	66	--	< .15	Do.
Dust-fertilizer spreader - - -	2.7	72	< .15	< .15	Do.
Carbaryl:					
Dust-fertilizer spreader - - -	1.5	49	.20-.47	--	Do.
Do. - - - - -	1.5	65	< .10	--	Do.
Heptachlor:					
Granules-power pack - - - - -	.25	51	< .15	< .30	Do.
Do. - - - - -	.75	201	.004-.14	.004-.01	Gas Chrom.
Do. - - - - -	1.00	51	< .15	< .30	Color.
Granules-aircraft - - - - -	1.33	236	.016	.004	Gas Chrom.
Do. - - - - -	1.50	77	< .15	< .30	Color.
Dust-aircraft - - - - -	1.50	77	< .15-.18	< .30	Do.
Toxaphene:					
Emulsifiable concentrate-					Total chlorine
power sprayer - - - - -	1.0	69	< .10	--	Do.
Do. - - - - -	2.0	69	< .10-.29	--	Do.
Do. - - - - -	3.0	69	< .10	--	Do.
Do. - - - - -	4.0	69	< .10	--	Do.
Do. - - - - -	6.0	69	< .10	--	Do.

1/ Results corrected for appropriate control samples, but not corrected for average percent recovery.

2/ The metabolite for aldrin is dieldrin and for heptachlor is heptachlor epoxide.

3/ This symbol indicates less than the lower limit of accuracy of the analytical method as used.

Where red clover was sprayed with 1 to 6 lb. of toxaphene per acre and harvested 69 days after treatment, only the 2-lb. plot carried measurable residues (0.29 p.p.m.). The presence of only one sample with measurable residue may possibly be explained by an overtreatment of one or more portions of the 2-lb. plot which could result in a higher residue sample.

Lima Bean Straw

The feeding of lima bean straw is not as widespread as the feeding of either red clover or range grass. The residue values obtained on lima bean straw treated with azinphosmethyl, dimethoate, disulfoton, phorate, and trichlorfon are presented in table 3.

Table 3.-Insecticide residues on lima bean straw

Formulation and method of application	Number of treatments	Pounds per acre (actual)	Days since last application	Residue in parts per million ^{1/}
<u>Azinphosmethyl:</u>				
Emulsion-foliage spray	3	1.5	44	7.8-20.3
<u>Dimethoate:</u>				
Emulsion-foliage spray	1	.5	37	< ^{2/} .10
Do. - - - - -	2	--	51	< .10
Do. - - - - -	1	1.0	37	< .10-.12
Do. - - - - -	2	--	51	< .10
Granules-soil - - - - -	1	.5	139	< .10
Do. - - - - -	1	1.0	do.	< .10
<u>Disulfoton:</u>				
Granules-soil - - - - -	1	.36	139	< .12
Do. - - - - -	1	.44	132	< .12-.56
Do. - - - - -	1	.66	132	< .12-.61
Do. - - - - -	1	1.00	139	< .12-.58
<u>Phorate:</u>				
Granules-soil - - - - -	1	.5	139	< .30
Do. - - - - -	1	1.3	do.	< .30
<u>Trichlorfon:</u>				
Emulsion-foliage spray	1	2.0	44	.02-.07

^{1/} Corrected for appropriate control samples, but not corrected for average percentage of recovery.

^{2/} This symbol indicates less than the lower limit of accuracy of the analytical method as used.

The persistence of azinphosmethyl on lima bean straw is illustrated by the finding of 7.8 to 20.3 p.p.m. of azinphosmethyl on straw from green plants that had been sprayed (foliage) with three treatments of 1.5 lb. of azinphosmethyl per acre, the last treatment 44 days before harvest.

Green lima beans treated with sprays (foliage) of 1/2 and 1 lb. of dimethoate per acre carried no measurable residues in the harvested dried straw, except 0.12 p.p.m. where 1 lb. per acre had been applied 37 days before harvest. When two sprays (foliage) at this concentration were applied, the last one 51 days before harvest, no measurable residues were found. Based on the above, it could be expected that if the 37-day time-interval had been extended to 51 days no measurable residues would have been found. Soil treatment 139 days before harvest with 0.5 and 1 lb. of dimethoate per acre did not result in measurable residues in the dry lima bean straw.

Soil treatment with 0.44 to 1.0 lb. of disulfoton granules per acre in a granular formulation applied 132 to 139 days before harvest produced measurable residues in the dry straw. Application of 0.36 lb. per acre did not result in measurable residues. In all treatments, there were some samples found with no measurable residues. In general the residue in the straw was approximately the same for the three higher rates of application.

Soil treatment with 0.5 and 1.3 lb. of phorate per acre, applied as granules, 139 days before harvest did not result in measurable residues of this material in the dry straw.

Two pounds per acre of trichlorfon applied as a spray (foliage) 44 days before harvest resulted in residues of 0.02 to 0.07 p.p.m. on the dry straw.

Range Grass

The treatment of large areas of range land for the control of grasshoppers is necessary in order to reduce the infestation and to preserve the range forage. Major requisites for treatment of range grass include: (1) control of the insects, (2) low cost per acre, and (3) persistence of the insecticide during the period of control but not long enough to render the range unusable for grazing purposes. Residues of Bomyl, carbaryl, diazinon, dimethoate, and naled on range grass are presented in table 4.

Bomyl was applied at the rates of 2 and 4 oz. per acre both as a water-diluted emulsion and as an oil concentrate spray. The sprays were applied by means of a modified turbine (Buffalo Turbine[®]) sprayer that permitted the covering of fairly large acreages in a minimum of time. The original, or zero day, deposits from the 2- and 4-oz. per acre water-emulsion spray and the 2-oz. per acre oil concentrate spray were very similar, whereas the deposit from the 4-oz. oil concentrate spray was approximately twice that of the others. Fourteen days after application, this difference was no longer significant; and after 28 days, the deposits remaining from the 4-oz. applications were 2.0 and 2.5 p.p.m. and that from the 2-oz. oil-concentrate was 1.6 p.p.m.

Carbaryl at 4 oz. per acre was applied as a water-diluted emulsion spray (foliage), both by modified (Buffalo Turbine) sprayer and aircraft. When 4 oz. of carbaryl per acre was applied by turbine sprayer, the original deposit (0-days) ranged from 18 to 50 p.p.m. When the same rate was applied by

Table 4.-Insecticide residues on range grass

Formulation and method of application	Ounces per acre (actual)	Days since last application and residue in parts per million ^{1/}									
		0	1	2	3-4	7-8	14	21	28		
Bomyl:											
Emulsion-turbine spray	2	15.5	5.4	--	3.1	1.6	--	--	--	--	
Do.	4	15.9	12.6	--	7.8	5.3	2.2	--	--	2.0	
Oil-concentrate turbine spray	2	17.6	24.3	--	11.7	5.6	3.0	--	--	1.6	
Do.	4	37.6	17.2	--	6.8	2.6	2.2	--	--	2.5	
Carbaryl:											
Emulsion-turbine spray	4	18.0	15.0	--	13.0	6.0	5.0	4.0	--	--	
Do.	4	50.0	43.0	--	36.0	16.0	7.0	6.0	--	--	
Do.	6	38.0	28.0	--	31.0	16.0	9.0	11.0	--	--	
Do.	6	44.0	43.0	--	41.0	14.0	7.0	4.0	--	--	
Do.	16	108.0	63.0	--	70.0	42.0	24.0	20.0	--	--	
Do.	16	115.0	100.0	--	106.0	38.0	16.0	14.0	--	--	
Emulsion-aircraft	4	34.0	28.0	--	20.0	19.0	--	--	--	--	
Diazinon:											
Emulsion-turbine spray	4	14.0	6.3	--	2.6	.8	.7	.4	--	--	
Do.	4	27.0	13.7	--	9.6	5.6	3.5	2.9	--	--	
Do.	6	34.8	15.6	--	11.4	6.2	4.8	3.3	--	--	
Do.	8	25.3	14.3	--	5.3	1.8	.8	1.1	--	--	
Dimethoate:											
Emulsion-turbine spray	1	3.5	1.8	--	1.1	0.4	0.3	0.4	--	--	
Do.	1	6.4	2.8	--	2.0	.7	.2	.1	--	--	
Do.	2	24.0	18.6	2.5	1.4	--	--	--	--	--	

Formulation and method of application	Ounces per acre (actual)	Days since last application and residue in parts per million ^{1/}							
		0	1	2	3-4	7-8	14	21	28
Dimethoate:									
Emulsion-turbine spray - - - -	3	15.6	--	--	2.8	2.8	1.7	2.0	--
Do. - - - - - - - - - -	3	22.8	7.3	--	8.3	1.7	1.1	1.0	--
Do. - - - - - - - - - -	4	68.6	50.8	30.1	15.7	1.7	--	--	--
Emulsion-TBM aircraft - - - -	1.7	2.5	1.8	--	1.5	2.2	--	--	--
Do. - - - - - - - - - -	3.4	14.2	3.9	--	2.0	1.4	--	--	--
Emulsion-Piper aircraft - - - -	3	81.6	62.0	--	10.1	17.3	12.6	4.7	--
Do. - - - - - - - - - -	3	17.9	12.5	--	15.0	13.0	9.3	4.9	--
Oil-concentrate-Piper aircraft -	3	86.0	49.6	--	40.2	29.6	49.6	27.4	--
Naled:									
Emulsion-turbine spray - - - -	4	.08	.06	--	--	--	--	--	--
Do. - - - - - - - - - -	4	3.0	.70	--	.13	.08	.06	--	--
Do. - - - - - - - - - -	6	1.7	.08	--	.06	--	--	--	--
Do. - - - - - - - - - -	6	1.0	.50	--	.15	.06	--	--	--

^{1/} Results corrected for the appropriate control samples, but not corrected for average recovery samples.

aircraft, the original deposit of 34 p.p.m. happened to be the average of the original deposit of the two turbine-applied plots. The zero day deposits increased as the dosage increased but not in mathematical proportion.

All plots were sampled 7 to 8 days after application. At this time interval from 44 to 65 percent of the original deposit had disappeared from the range grass. Where 4, 6, or 16 oz. per acre was applied as a water emulsion by turbine sprayer, the rate of loss of the original deposit at 21 days after application was 83, 81, and 85 percent, respectively.

Diazinon was applied at rates of 4, 6, and 8 oz. per acre by modified turbine (Buffalo Turbine) sprayer. The zero day deposits did not increase in the same proportion as the rates of application. The initial deposit resulting from the 8-oz. application was slightly less than the initial deposit found on one of the 4-oz. treated plots. The rate of disappearance of diazinon was rather rapid, with an average of 72 percent of the initial deposit lost in the first 3 to 4 days. Seven to eight days after application, an average of 86 percent of the original deposit had been lost from the range grass. Twenty-one days after application, an average of 92 percent or more of the original residue had disappeared from the grass.

Dimethoate was applied as a water-emulsion and an oil-concentrate spray. Applications were made by turbine sprayer and two types of aircraft. Where 1, 2, 3, and 4 oz. per acre were applied as a water-emulsion spray by ground rig, the original deposits on range grass did not correlate with the increase in dosage per acre. Where the water-emulsion spray was applied by TBM aircraft, doubling the dosage resulted in almost a sixfold increase in original deposit. When 3 oz. per acre was applied by aircraft as an emulsion formulation, the original deposit on the two plots varied almost fivefold. The original deposit resulting from 3 oz. per acre applied by aircraft as an oil-concentrate was nearly the same as the original deposit in one of the plots when the same amount was applied by the same type aircraft as an emulsion.

Two rates of application were made by use of larger aircraft. When 1.7 oz. per acre was applied as an emulsion, the original deposit was considerably lower than when 1 and 2 oz. per acre were applied by ground rig. The residue levels found 1, 3 to 4, and 7 to 8 days after application of the 1.7-oz. rate indicate that the original deposit figure is probably in error. When 3.4 oz. per acre, as an emulsion, were applied by aircraft, the original deposit corresponded fairly well with the original deposit found on the plots treated with 3 oz. per acre by ground rig. Where more than one plot was treated with the same rate per acre, the original deposits ranged from 1.4- to 4.6-fold. On the basis of formulation and method of application, the highest average deposit per ounce of active material was obtained with the oil concentrate applied by aircraft.

Fourteen days after application, from 42 to 97 percent of the original deposit had been lost from the range grass. Seven to eight days after application, the residue loss from the grass ranged from 66 to 98 percent when two plots were disregarded. The data obtained on these two plots, 1.7-oz. emulsion applied by TBM and 3 oz. of emulsion formulation applied by Piper aircraft, indicate that the original deposit figures are probably in error by

being lower than the actual deposit present. This statement is based on the calculated rate of loss per sampling period for each plot. With the exception of the two plots indicated above, the rate of loss of the original deposit for each plot agrees very well.

The treatment of range grass with 4 and 6 oz. of naled per acre resulted in low original deposits. The rate of loss of naled from the range grass was rapid, with 78 percent of the original deposit lost in the first 24 hours and 95 to 99 percent lost in 3 to 7 days.

When the residues from all treatments for any one insecticide were averaged at each sampling time and the percentage of loss of the original average deposit calculated, it was found that naled had the fastest rate of disappearance. Diazinon and Bomyl were lost from the range grass at comparable rates, followed by dimethoate and carbaryl with similar disappearance curves.

SUMMARY

Residue determinations of one carbamate, three chlorinated hydrocarbon, and eight organic phosphate insecticides on red clover, lima bean straw, and range grass were conducted over a period of 8 years. The toxicants were applied as dusts, granules, and sprays (foliage). When red clover was treated with aldrin, carbaryl, heptachlor, and toxaphene harvest residues ranged from <0.10 p.p.m. to 0.47 p.p.m. - Lima bean straw treated with dimethoate, phorate, and trichlorfon carried harvest residues of 0.10, 0.30, and 0.02 to 0.07 p.p.m., respectively. Residues of 13.7 p.p.m. (average) were found on the azinphos-methyl-treated lima bean straw, and from <0.12 to 0.61 p.p.m. on disulfoton-treated lima bean straw. Measurable residues of Bomyl, carbaryl, diazinon, and dimethoate were found on range grass when sampled at varying intervals after application. Where naled was applied, 95 to 99 percent of the zero day residue had dissipated in 7 days.

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